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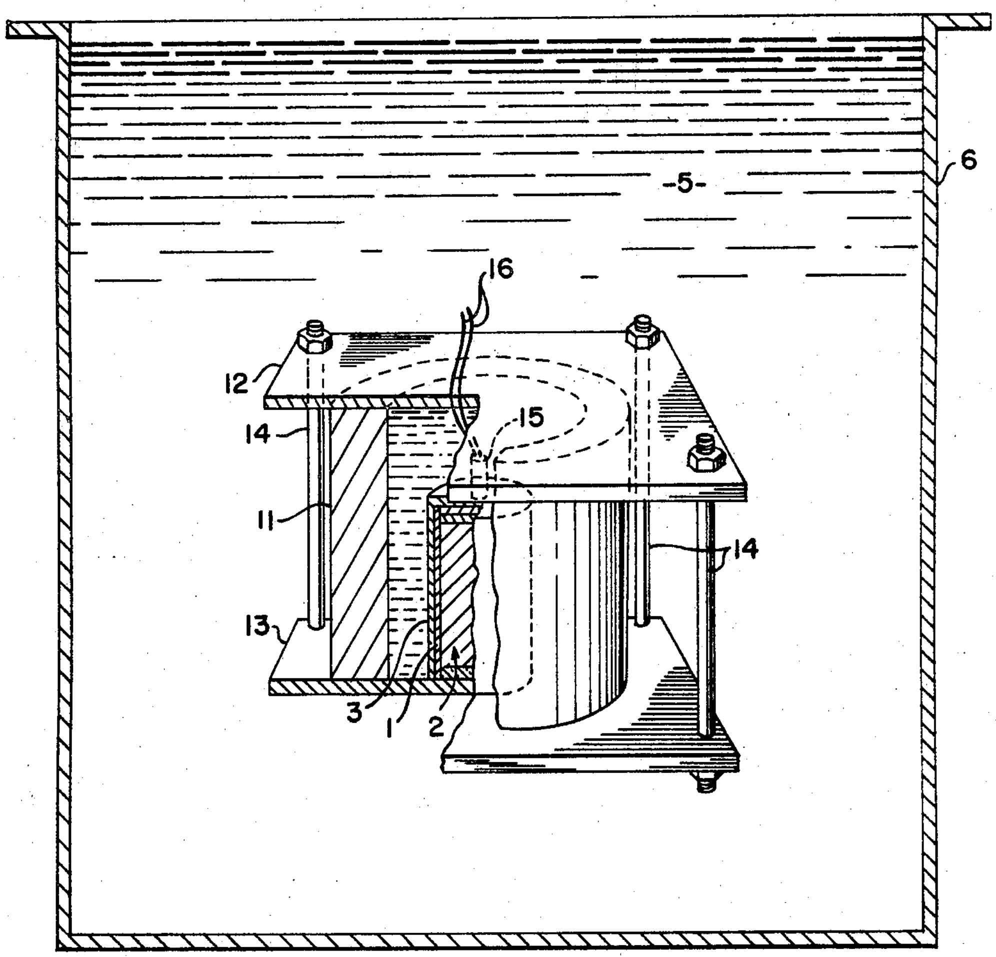

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1

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ELECTRIC RESISTANCE HEATER AND METHOD OF MAKING

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ABSTRACT OF THE DISCLOSURE

A method of making an electrical resistance heater from silicon carbide particles in which a body of such particles is closely packed in a sealed container and subjected to explosive compaction. The container is then removed and the heater element is subjected to further heating to provide a substantially completely metallurgically bonded resistance heater of silicon carbide particles.

This invention relates generally as indicated to an electrical resistance heater and to a method of making such heaters, and more particularly relates to such elements which are produced by explosive compaction.

Following the discovery of silicon carbide (SiC) and of a method for artificially making the same as a commercial product, it has, as is well known, entered into wide use as an abrasive material. Also it was further early discovered (see U.S. Patent No. 650,234, dated May 22, 1900) that by compressing a mass of such silicon carbide in granular or powdered form into a desired shape and subjecting the resulting article to a high temperature, it would be useful as an electrical conductor, particularly if graphite or its equivalent was intermixed with the grains or particles of silicon carbide. In the interval electrical conductors of this type have come into extensive use as the heating elements in electric furnaces for operation at temperatures as high as 1500° C. or higher in ordinary air atmosphere.

Where thus used as electrical resistance heaters, the component materials are ordinarily pressed into bodies of elongated form, e.g., rods, and suitable provision is, of course, made for attaching the ends thereof to conductor terminals in the required electric circuit. The intermediate or main portion of the heater element thus provided becomes the so-called "hot zone," while each end constitutes the so-called "cold zone" of the element. For obvious reasons it is desirable that the electrical conductivity of such cold ends be relatively high compared with that of such hot zone, and, accordingly, that the composition thereof be varied from that of such hot zone; and various methods have been proposed for effecting this result, as by impregnating such ends with a material consisting substantially of silicon or by immersing the same in a suspension of colloidal graphite.

We have made the surprising discovery that, despite the refractory nature of the material, when a body of silicon carbide is subjected under proper conditions to explosive compaction, a superior resistance heating element can be obtained. Generally described, such explosive compaction procedure includes the steps of confining the powder material in a container, placing an explosive charge closely adjacent to the surface of the latter, and then detonating the explosive charge. Accordingly, one principal object of the present invention is to produce an electrical resistance heating element of the character described by initially forming the same by explosive compaction, instead of by ordinary methods of compression, so that an element having minimal voids is obtained. At the same time, by thus compacting granular mixtures of

2

silicon carbide with different proportions of resistance-modifying additives in the cold ends and the hot sections, the desired differences in conductivity in the element can be obtained without the necessity of any supplemental impregnation treatment of the ends.

We have further discovered that by heat treating such explosively compacted silicon carbide heating elements, still further improved properties can be achieved as a result of the vaporization of the silicon phase which permeates the structure.

To the accomplishment of the foregoing and related ends, the invention, then, comprises the features hereinafter fully described and particularly pointed out in the claims, the following description and the annexed drawing setting forth in detail an illustrative embodiment of the invention, this being indicative, however, of but one of the various ways in which the principle of the invention may be employed.

In said annexed drawing, the figure is a partially sectioned diagrammatic view in perspective of an assembly adapted for explosive compaction of silicon carbide powders in accordance with the present invention.

Electrical resistance elements composed of silicon carbide are usually made in the form of rods and the description of the apparatus and procedural steps which follow relate to the production of elements of the indicated form. It will be understood, however, that the dimensions given are merely illustrative; among other things, the length and diameter of the element may obviously be varied, depending upon the particular type of heater, e.g., electric furnace, in which the resistor is to be employed. An important consideration is that such rods be dense, so as to substantially eliminate any tendency to produce arc cracking, and also that the resistivity of the rods, particularly in the "hot zone," be uniform. It is also essential that the resistivity of the rod should be such that it can be resistance heated at the voltage and amperage available with the standard electric furnace power source. To this end it has been found desirable to incorporate in the silicon carbide a resistance modifying additive, sometimes referred to as a doping agent. By incorporating a different amount of such agent in the ends of the rod from that incorporated in the intermediate portion, such ends are rendered still more highly conductive, so that when in use, the heating effect is substantially confined to such intermediate portion or hot zone of the rod.

Furthermore, the type of material used to contain the powder during compaction has a definite effect on the character of the compacted rod. Likewise, the procedure employed to remove the container material from the compacted rod affects the character and thus the functioning of the latter.

Various types of silicon carbide in powdered form are available for use in making our improved resistor elements, for example Norton "Green," Carborundum grit grade and Carborundum "Carbotronic" grade. In general, the particle size of such silicon carbide may be in the range of submicron size (less than about 1 micron in diameter) to 20 mesh U.S. Standard sieve size, with the preferred size range being from about 60 to 150 mesh.

The selected powder material is generally prepared for explosive compaction by vibratory packing the same into a metal tube of proper dimensions, evacuating the tube and then sealing by electron beam welding-in the final end plug. Such tube is then tightly wrapped in an envelope of sheet explostive, such as Du Pont "Deta Sheet" (although other commercially available explosives having similar explosive characteristics may also be used), of the desired charge density, an electric blasting cap being affixed to such charge at one end of the container.

The charge density of the explosive charge may be varied considerably depending on the container material and the diameter of the silicon carbide rods. When a ½ inch rod is being produced, the charge density will generally be from about 2–5 gms./in.², and preferably from 3.5 to 4.5 gms./in.². Such charge densities have been found quite satisfactory to produce silicon carbide rods of the desired density which will generally be from about 93 to 95 percent or greater of the theoretical apparent specific gravity of 3.10. The rods should therefore have a specific gravity of about 2.88 to 3.04 or higher so that the open porosity of the rods will be as minimal as is economically possible to provide increased electrical continuity.

The container with its charge thus prepared and with the explosive material properly applied thereto may then be submerged, as is the conventional procedure, in a tank of water and the explosive charge thereupon detonated. However, a preferable arrangement is that illustrated in the drawing wherein the container **1** with its contents **2** and surrounding explosive charge **3** is placed in a specially constructed pressure retaining housing which is in turn thus submerged in a suitable open body of water **5** in a tank **6** of appropriate size.

As illustrated, such housing will be seen to comprise a cylindrical member **11** normally open at both ends, but adapted to be closed by plates **12** and **13** which are drawn together by clamp bolts **14** is the assembled condition of the housing. The interior diameter of the cylinder **11** is substantially larger than that of the container **1** and of greater longitudinal extent, the space thus provided being filled with water just as is the tank **6**. Attached to the upper end of the explosive charge **3** is an electric blasting cap **15** to which are connected suitable insulated leads **16** that extend through the upper plate **12** and beyond the body of water in tank **6**, whereby electric current may be conducted for firing the blasting cap **15**.

The assembly just described may be suspended in any suitable way in the larger body of water within tank **6**, the explosive charge detonated, the housing removed from the pressure transmitting medium and the container **1** in turn removed from the housing. By placing the container within the housing as above described, the pressure generated by the explosion is unloaded slowly, reducing the slope of the unloading curve and thus assisting in the prevention of cracks in the compacted element.

Following explosive compaction, the metal container surrounding the compacted powder will be removed so as to leave exposed the resulting resistor element. Where such container is mild steel, removal thereof may conveniently be effected by leaching in a solution of 50 volume percent water and 50 volume percent nitric acid. Alternatively the container may be removed by mechanical means.

As an alternative to the housing arrangement for carrying out the explosive compaction step, the explosively wrapped container **1** with attached detonating cap **15** and electric leads **16** may, as previously indicated, be submerged directly in a tank of water.

Because of the high electrical resistance of rods or other resistor elements made from pure silicon carbide by the hereinbefore described methods of explosive compaction, it may be desirable to incorporate with such carbide a resistance modifying additive. Thus, significant increases in the conductivity of the element are obtained by the addition of, for example, from about 2.5 to 5 volume percent of a commercial "doping agent" such as silicon metal, BN, $MoSi_2$, ZrC, B_4C, TiC, and a mixture composed of 86 volume percent ZrB_2—12 volume percent $MoSi_2$—2 volume percent BN. The particle size of the modifying agents should, of course, correspond with the selected sizing of the silicon carbide grains. Additions of about 3 volume percent of these doping agents prove extremely satisfactory in producing rods which are effective heaters when connected to a standard electric furnace power source. Such additions, furthermore, reduce the frequency of formation of arc cracks and increase the strength of the as-compacted rods.

It has furthermore been found that by varying the amount of the addition of such resistance modifying additive or doping agent, a compacted element or rod can be produced possessing integral hot and cold zones. By way of example, for making the end or cold zone portions of the element, a roll blended mixture of 60 volume percent silicon carbide—40 volume percent doping agent may be employed and a 97 volume percent silicon carbide—3 volume percent doping agent for the intermediate hot zone. Using silicon metal and $MoSi_2$ as the doping agents, the container is mounted on a vibratory packer and the cold zone mixture introduced initially, then the hot zone mixture, and finally more of such cold zone mixture, each until the desired length is achieved. The container thus filled is then subjected to explosive compaction, preferably under water, without the use of a pressure retaining housing. As a result of the foregoing procedure, high-density silicon carbide heater rods may be directly produced with integral cold zone ends and an intermediate longer hot zone.

The bonding together of the particles which compose a silicon carbide heater rod thus produced may be improved to obtain in effect a more complete, metallurgical bonding rather than a mechanical-metallurgical bonding by subjecting the same to a further suitable heat treating step. While it has been found that such bonding in the hot zone area may be obtained by resistance heating of the rod, such as would result from actual use thereof as a resistor element, it is preferred to heat treat the same by externally applied heat for a period of from about 2 to 8 hours at a temperature varying from approximately 2100° to 3200° F. with the preferred range being from about 2500° to 2700° F. when a silicon modifying agent is used, as described previously, although the temperature range may be greater or lower depending upon the type of modifying agent used, the nature of the furnace atmosphere, and whether a vacuum is used. Such heating will be desirably conducted in an air-free atmosphere, e.g., the noble gases such as argon, helium, neon, etc., or low molecular weight carbon bearing gases, such as carbon monoxide, methane, ethane, propane, etc., to avoid the formation of silica, which possess a resistivity higher than that of silicon carbide and thus would counterbalance the decrease in resistivity achieved by the particle bonding obtained during the heat treatment. The silica would also collect in and fill the pores of the rods. Since it has a higher coefficient of thermal expansion than silicon carbide, the rod will rupture during heating after the pores are so filled. In order to prevent such silica formation, this heat treatment may also be carried out in a vacuum with the result that as the silicon vapor, derived from the silicon additive, comes in contact with the silicon carbide particles, it will react with the excess carbon therein to form additional silicon carbide. In so doing it also acts to further bond the particles together by producing a silicon carbide-silicon carbide-silicon carbide bond which is extremely strong.

Reference has hereinabove been made to mild steel as a material suitable for use in forming the metal container in which the silicon carbide may be explosively compacted. In certain respects aluminum, specifically 3S aluminum, has been found a more satisfactory metal for this purpose, in that an improvement in the visual appearance of the resulting rod is obtained, irrespective of whether in the step of explosive compaction the previously described pressure retaining housing is employed. Furthermore, the desired as-compacted density of the rods can be achieved with a lower charge density, viz., 4 g./in.², when using such 3S aluminum containers (aluminum being much softer than mild steel) than when using mild steel containers when a charge density of about 4.5 g./in.² is necessary to produce rods sufficiently dense to have satisfactory mechanical and electrical properties. It is believed that the improved characteristics achieved with such 3S aluminum containers are due to a more amenable match of acoustical properties between the aluminum and silicon carbide than that encountered between mild steel and the silicon carbide, with a resulting reduction in the tendency for arc cracking during compaction.

Where aluminum instead of mild steel is used as the material for the container in the explosive compaction step, such container may likewise be removed by leaching, using agents other than the previously described nitric acid solution. Specifically, such removal may be effected by leaching in NaOH followed by a water rinse, leaching in H_2SO_4 followed by a water rinse, or leaching in HCl followed by a water rinse. After leaching, the specimens are then dried. It has been found that a glassy phase consistng of low melting point complex sodium and/or aluminum silicates will form on the surface of the resistors following heat treatment at elevated temperatures in air when NaOH leaching agents are used. Since no such formation occurs with the HCl agents, they are the preferred leaching agents.

The container, whether mild steel or aluminum, may also be removed by melting the same off the rod with an acetylene torch. This procedure is somewhat more rapid; however, the amount of heat required to melt the mild steel container may result in an undesirable reaction between the same and the silicon carbide. Likewise, in thus melting off aluminum containers, a thin film of aluminum tends to remain on the surface of the rod, and such film, being a good conductor, tends to prevent the rod from being heated by self resistance.

The following results, obtained by testing a series of 12 in. long silicon-doped silicon carbide rods of ½ inch diameter made in accordance with this invention, will serve to illustrate the striking and significant improvement which has been achieved in electrical resistance heaters. The rods thus tested, comprising integral hot and cold zones, were made by explosive compaction of Carbotronic grade silicon carbide powder of 80–100 mesh particle size, blended in a roll blender with silicon metal doping agent and loaded into 3S aluminum containers to produce specimens comprising a hot zone, 6 inches in length, of 97 volume percent silicon carbide—3 volume percent silicon metal and cold zones of 60 volume percent silicon carbide—40 volume percent silicon metal. The containers were wrapped with a sheet of Du Pont "Deta Sheet" of 4.0 gms./in.^{2} charge density. The containers were removed by leaching in a 50–50 volume percent HCl-water solution followed by a water rinse and drying for 1 hour at 180° F. and 8 hours at 350° F. in a circulating air drying oven. The rods were then heat treated for 4 hours at 2550° F. in a vacuum. Such rods were then subjected to transverse rupture tests to determine their strength, such tests being conducted in a standard tensile testing machine using a four point loading with a 2-inch span between the upper points through which the load was applied and a 3-inch span between the lower points. Table I sets forth the results of such tests, the transverse rupture strength in all cases, whether taken at the hot zone—cold zone junction or in the hot zone, being very much greater than obtainable with any commercially available silicon carbide resistor, viz.:

TABLE I

Point of test	Diameter (in.)	Maximum applied load (lbs.)	Transverse rupture strength (p.s.i.)
Hot zone-cold zone junction	0.520	381	6,927
Do	0.519	390	7,270
Do	0.524	480	8,548
Hot zone	0.521	690	11,500
Do	0.521	490	8,850
Do	0.515	755	14,180
Do	0.520	570	10,300
Do	0.510	672	12,590
Do	0.520	406	7,382
Do	0.515	436	7,927

To demonstrate the superiority of the silicon carbide resistance elements produced in accordance with this invention, commercially available silicon carbide heaters were subjected to the same transverse rupture tests as described above, with the results shown in Table II. A comparison of the results of Tables I and II indicate that the heaters of this invention possess considerably greater rupture strength than the present commercial items.

TABLE II

Point of test	Diameter (in.)	Maximum applied load (lbs.)	Transverse rupture strength (p.s.i.)
Hot zone-cold zone junction	0.513	262	4,990
Do	0.506-OD 0.225-ID	138	1,551
Do	0.505-OD 0.227-ID	117	1,368
Hot zone	0.517	158	2,940
Do	0.514	228	4,280
Do	0.508-OD 0.228-ID	124	1,389
Do	0.502-OD 0.210-ID	159	1,955

Resistance heater rods substantially identical with those employed in carrying out the foregoing mechanical tests were also tested as to their electrical resistance and durability in use, viz., by being connected with suitable leads to a 220 volt-60 amp. power source and passing an electric current through the rods. The average power requirements necessary to resistance heat such rods to a temperature of 1800° F. was found to be 37 volts and 17 amps. As indicating the increased life expectancy of such rods under conditions of use, a group thereof was installed in a small furnace and electrically connected in series to a 220 volt-60 amp. power source and heated continuously at 1800° F. for a period of three months. The power density required to maintain this temperature remained constant at 28 watts per in.^{2}. Upon removing the rods at the end of such test period, no deleterious effects in their appearance could be detected by visual examination.

The increased strength of the explosively compacted heater rods is attributed to the silicon carbide-silicon carbide-silicon carbide bonding mechanism as compared with the silicate or silicon nitride bonding mechanism used with commercial rods and to the increased density (93 to 95 percent or greater of the theoretical apparent specific gravity) of explosively compacted heater rods over that of commercial heaters, which are normally about 75 percent of the theoretical apparent specific gravity. It is also expected that the increased density of the explosively produced heater rods will increase their operating life since they possess virtually no porosity in which silica can form and collect to increase the resistivity of the rod and eventually cause its failure.

From the foregoing it will be evident that by utilizing an explosive compaction technique we are able to produce a much superior silicon carbide resistor element, i.e., one that can be satisfactorily employed as an electric resistance heater in electric furnaces and the like, in that not only is the element thus produced substantially free of voids but of high density. Furthermore, by employing such explosive compaction technique, it is rendered possible to incorporate in the element varying amounts of selected additives such as are required to provide an element with the required resistance characteristics for such indicated use, specifically an element the ends or so-called "cold zones" of which are of greater conductivity than the intermediate heating or so-called "hot zone." Thus we are able to dispense with subsequent impregnation of the element and like unsatisfactory procedures to produce an element that will function in the manner required. At the same time, an element is obtained, in which the composition throughout the several zones will be uniform and so the life, as well as the performance characteristics, of the element increased.

Other modes of applying the principle of our invention may be employed, instead of the one explained, change being made as regards the product and method herein disclosed, provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

We therefore particularly point out and distinctly claim as our invention:

1. A method of making an electrical resistance heater element from silicon carbide particles, the steps which comprise closely packing a body of such particles in a sealed metal container, subjecting the latter with contents to explosive compaction to provide an element having a minimum specific gravity of at least about 2.88, removing such container, and then subjecting the compacted body to an elevated temperature in the absence of air to produce a substantially complete metallurgical bonding of the silicon carbide particles.

2. The method of claim 1 in which the compacted body is subjected to a temperature in the range of approximately 2100° F. to 3200° F. in vacuum.

3. The method of claim 2 in which the temperature range is from approximately 2500° F. to 2700° F.

4. The method of claim 2 in which the compacted body is subjected to said elevated temperature for a period of from about 2 to 8 hours.

5. The method of claim 1 in which the compacted body is heated in the presence of a noble gas.

6. The method of claim 1 in which the compacted body is heated in the presence of a low molecular weight carbon bearing gas.

7. The method of claim 1 in which a resistance modifying additive is admixed with such silicon carbide particles prior to packing in such sealed container.

8. The method of claim 7 in which the amount of such resistance modifying additive is greater in the end portions of such body than in the intermediate portion thereof.

9. A method of making an electrical resistance heater element from silicon carbide particles, the steps which comprise closely packing a body of such particles in a sealed metal container, subjecting the latter with contents to explosive compaction to provide an element having a minimum specific gravity of at least 2.88, controlling the unloading rate during such explosive compaction, removing such container, and subsequently subjecting the compacted body to an elevated temperature in the absence of air to produce a substantially complete metallurgical bonding of such silicon carbide particles.

10. The method of claim 9 in which the explosive compaction is effected in a pressure retaining housing whereby the pressure generated by such explosion is unloaded in a controlled manner to reduce the slope of the unloading curve and assist in the prevention of cracks in the compacted element.

11. The method of claim 8 in which the amount of such additive in the end portions of such body is approximately 40 volume percent and in the intermediate portion is approximately 3 volume percent.

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